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Exchange of Lithium Isotopes in the System Aqueous Lithium Chloride Solution – Lithium and Aluminum Double Hydroxide

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Abstract

Isotopic exchange between the aqueous solution of lithium chloride containing ⁶Li isotope and the chloride form of double aluminium and lithium hydroxide synthesized from different aluminium hydroxide species was studied. It was demonstrated that the dependence of the level of isotopic exchange F(t) on time at the initial regions (the exchange level being less than 40 %) for the samples of double hydroxide obtained from crystalline gibbsite can be described by a diffusion equation: $F(t) = (4/r_0\pi^{1/2})D^{1/2}t^{1/2}$. The diffusion coefficients of lithium are comparable with the coefficients of self-diffusion of singly charged alkaline ions in skeletal aluminosilicate such as mordenite. The exchange level for the samples of double hydroxide obtained from mechanically activated aluminium hydroxide under comparable experimental conditions is an order of magnitude greater than the exchange level for the samples synthesized from gibbsite. This is likely to be connected with a higher dispersion level of double hydroxide synthesized from mechanically activated aluminium hydroxide.

Key words: isotopic exchange, lithium hydroxide, aluminium hydroxide

INTRODUCTION

The modern industrial technology lithium isotope separation is based on the amalgam method [1]. A high toxicity of this process determines the urgency of research works devoted to the development of methods for the separation of lithium isotopes without the use of mercury. Among the chemical methods of isotope separation there are well known techniques based on the use of oxygen-containing [2, 3] and nitrogen-containing crown ethers [4], organic [5], and inorganic ion exchangers [6?9]. High separation factors (1.05?1.06) were obtained *via* using the oxygen and nitrogen crown ethers with small size cavity [2]. The advantages of crown ethers consist in the possibility of applying them onto different high-porosity granular media. This allows one to use the chromatographic methods for the separation of isotopes with no significant reduction of the separation factors. Unfortunately, the high cost of crown ethers causes their wide application to be limited. Furthermore, high separation factors are observed in the case of using flammable and toxic organic solvents (methanol, chloroform, *etc.*) as eluents.

Among the inorganic ion exchangers with a high separation factor one could consider manganese oxide compound [6, 7], titanium phosphate [8], antimonic acid [9]. The main disadvantage of the mentioned compounds consists in a complicated method employed for their synthesis. It should be noted that high separation factors are inherent in those ion exchangers (manganese oxides, antimony acid,

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etc.), wherein the lithium cations under exchanging are located in octahedral and tetrahedral cavities, comparable in size to the lithium cations. Just as it is in the case of crown ethers, owing to a small size of voids the transition of lithium ions from solution to the solid phase results in significantly changing its environment, which provides a sufficiently high rate of lithium isotope separation.

Another interesting class of inorganic compounds is presented by aluminium hydroxide that was found to exhibit sufficiently high rates of lithium isotope separation [10, 11]. The reaction of aluminium hydroxide with lithium salts leads to the formation of an anionic form of layered double hydroxides (LDH) of lithium and aluminium [LiAl₂(OH)₆]_nX · mH₂O (Li–Al–X LDH) [12]. Thus, the process of the separation of isotopes, to all appearance, is connected to the process of isotopic exchange between liquid and solid phases according to reaction

 $[^{6}\text{LiAl}_{2}(\text{OH})_{6}]_{n}\text{X} \cdot m\text{H}_{2}\text{O} + {}^{7}\text{Li}^{+}$

 $\leftrightarrow [^{7}\mathrm{LiAl}_{2}(\mathrm{OH})_{6}]_{n}\mathrm{X}\cdot m\mathrm{H}_{2}\mathrm{O} + {}^{6}\mathrm{Li}^{+}$

In the structure of double aluminium and lithium hydroxide the lithium cations are located in octahedral voids formed by hydroxide ions. The size of these voids is comparable to the size of the lithium cation, so the lithium isotopic exchange between the liquid and the solid phases is also connected with fundamental changes in the nearest circumference of lithium cations. To all appearance, just this could determine a rather high separation factor.

For the implementation of lithium isotope separation on aluminium hydroxide it is important to have not only a certain value of the separation factor, but also a high rate of isotopic exchange. Despite a great amount of studies concerning the lithium isotopic exchange [13], an overwhelming majority of research works is devoted to measuring the coefficient of isotope separation, whereas the isotopic exchange kinetics is studied to an insignificant extent. The aim of the present work was to study the kinetics of lithium isotopic exchange in aqueous solutions of LiCl-Li-Al-C LDH.

EXPERIMENTAL

For the study of isotopic exchange we used lithium chloride aqueous solutions, enriched with isotope Li-6 (90 at. %). The synthesis of Li-Al-Cl LDH was performed using an aqueous solution of lithium chloride with the content of isotope Li-6 close to the naturally occurring one. For the process of isotopic exchange we used two types of Li-Al-Cl LDH samples. The first type samples were synthesized via treating the monofraction (5-10 µm) of crystalline aluminum trihydroxide by a concentrated aqueous lithium chloride solution (20 mass %) at 90 °C and the reaction duration amounting to 6 h. The aluminium trihydroxide monofraction was obtained under a short-time (30 s) grinding of crystalline gibbsite produced at the Achinsk Alumina Refinery using an AGO-2 activator in an aqueous medium with subsequent sizing the products of grinding by means of a KC-1 centrifugal classifier (designed at the ISSCM of the SB RAS, Novosibirsk).

The particles of gibbsite represent the fragments of hexagonal plates or (more rarely) prismatic bars. The solid phase formed in the reaction between aluminium hydroxide with lithium chloride was analyzed for aluminium, lithium and chlorine. Lithium was determined by means flame photometry, aluminium was determined using complexometric method; chloride ion was analyzed with the help of mercurimetric method. The XRD phase analysis data (DRON-3, CuK_{α} radiation) indicate the formation of well-crystallized aluminium and lithium double hydroxide, as well as gibbsite impurity absence. The results of the chemical analysis of the solid for aluminium, lithium and chlorine indicate the formation of aluminium and lithium double hydroxide with the composition close to $[LiAl_2(OH)_6]Cl \cdot nH_2O$. According to optical microscopy data, the morphology of the double hydroxide is close to the morphology of the initial aluminium hydroxide, particles the size of the most of particles is within the range of $5-10 \,\mu\text{m}$.

The interaction between Li-Al-Cl LDH with the aqueous lithium chloride solution, alongside with the isotopic exchange process could be accompanied by lithium chloride deintercalation process, whereby we investigated the stability of this compound in aqueous solutions of lithium chloride with various concentrations (20-80 g/L) at different temperature values (50-90 °C). The interaction time in

all the cases was equal to 6 h. The chemical composition of the resulting products indicates that there is a partial deintercalation of lithium chloride from Li-Al-Cl LDH observed. The XRD profiles of the products formed in the course of deintercalation are identical to the XRD profile of the initial $[LiAl_2(OH)_6]Cl \cdot nH_2O$. Basing on this fact one could assume that under the experimental conditions, the solid solution formed is of interstitial type based on the initial structure of the Li-Al-Cl LDH. In this connection, for the isotopic exchange process we used and an interstitial solid solution based on the compound with the chemical composition close to $[Li_{0.92}Al_2(OH)_6]Cl_{0.92} \cdot mH_2O$ rather than an ideal double hydroxide composition.

For the synthesis of the second type samples we used XRD amorphous aluminium hydroxide produced in the course of the activation of the initial gibbsite in an AGO-2 planetary type activator at the acceleration equal to 40g and the activation time amounting to10 min. The treatment of mechanically activated aluminium hydroxide was carried out also using a 20 % aqueous solution of lithium chloride at 90 °C during 6 h. The XRD profile of the compound synthesized exhibits broadened reflexes, whose interplanar distances are inherent in the Li–Al LDH (7.56, 3.83 Å). The chemical composition of the compound synthesized corresponds to formula [Li_{0.66}Al₂(OH)₆]Cl_{0.66} \cdot nH₂O.

For the isotopic exchange process we used an aqueous solution of lithium chloride (40 g/L) enriched by isotope Li-6 (90 %). Monitoring the isotopic exchange was performed *via* measuring the concentration of isotope Li-7 in aqueous solution with the use of NMR method. As the samples for NMR spectra calibration we used lithium chloride aqueous solutions with known isotopic composition. For the registration of NMR spectra we used a DRX-500 NMR spectrometer.

RESULTS AND DISCUSSION

Studying the kinetics of lithium isotope exchange in the system of LiCI- $Li_{0.92}AI_2(OH)_6]CI_{0.92} \cdot nH_2O$

Table 1 demonstrates data concerning the isotopic composition of solutions obtained at different temperature values and different interaction time in the system of LiCl– $\text{Li}_{0.92}\text{Al}_2(\text{OH})_6$]Cl_{0.92} · $n\text{H}_2\text{O}$. In order to determine the level of isotopic exchange F(t) we used expression

 $F(t) = (\alpha(t) - \alpha(0))/(\alpha(\infty) - \alpha(0))$ (1)where $\alpha(t)$ is the content of isotope Li-7 in the solution at time (t),%; $\alpha(0)$ is the content of isotope Li-7 in the solution at the beginning of the exchange process; $\alpha(\infty)$ is the content of isotope Li-7 in the solution under equilibrium. Basing on the form of the kinetic curves, we suggested that the equilibrium condition could be reached at 80 °C during 10 h. The processing of kinetic data concerning the isotopic exchange was performed with an assumption that the isotopic exchange process occurs owing to the process of two-dimensional diffusion from a limited volume of solution into the particles of the solid phase those can be described as discs the same radius r_0 . In this case, for small values of F(t) [14]: $F(t) = kD^{1/2}t^{1/2}$ (2)

where $k = 2A/(W\pi^{1/2})$ (*A* is the surface of the body, *W* being the body volume). Substituting the values **??** of parameters *A* and *W*, we obtain: $k = 4/r_0\pi^{1/2}$. Consequently,

$$F(t) = (4/r_0 \pi^{1/2}) D^{1/2} t^{1/2}$$
(3)

The graphic analysis of F(t) depending on $t^{1/2}$ demonstrates that when the exchange level is lower than 40 % the F(t) value depends on the $t^{1/2}$ in an almost linear manner. Substituting into eq. (3) the value $r_0 = 5 \cdot 10^{-4}$ cm, t = 3600 s, we obtain that the values of D are varied within the range from $0.3 \cdot 10^{-12} - 3.2 \cdot 10^{-12}$ cm²/s depending on the temperature of isotopic exchange. It should be noted that the values obtained for the lithium diffusion coefficient are comparable to those for the self-diffusion coefficient of singly charged alkali ions in skeletal aluminosilicate such as mordenite [15].

Studying the kinetics of lithium isotope exchange in the system of LiCI– [Li_{0.66}Al₂(OH)₆]Cl_{0.66} · nH₂O

Table 1 also demonstrates data concerning the isotopic composition of lithium chloride solutions and the isotopic exchange level after the interaction between aqueous LiCl solutions and $[Li_{0.66}Al_2(OH)_6]Cl_{0.66}$ nH_2O at different temperature values and reaction time. The level of isotopic exchange for double hydroxide synthe-

<i>t</i> , h	$t^{1/2}$, h	α, at. %								
		$T = 40 ^{\circ}\mathrm{C}$	F(t)	$T = 50 \ ^{\circ}\mathrm{C}$	F(t)	$T = 70 ^{\circ}\mathrm{C}$	F(t)	$T = 80 \ ^{\circ}\mathrm{C}$	F(t)	
		$\mathbf{LiCl}{=}[\mathbf{Li}_{0.92}\mathbf{Al}_{2}(\mathbf{OH})_{6}]\mathbf{Cl}_{0.92} \cdot n\mathbf{H}_{2}\mathbf{O}$								
0	0			9.4	0	9.4	0	9.4	0	
0.5	0.7			13.3	0.12	15.6	0.19	20.8	0.36	
1	1.0			14.1	0.15	17.9	0.27	25.0	0.49	
2	1.41			16.1	0.21	22.0	0.40	28.9	0.61	
4	2.0			17.9	0.27	24.3	0.47	30.9	0.68	
6	2.45			19.7	0.32	28.7	0.61	39.8	0.96	
10	3.16			-	-	34.7	0.80	41.2	1.0	
				$\mathbf{LiCl}{=}[\mathbf{Li}_{0.66}\mathbf{Al}_{2}(\mathbf{OH})_{6}]\mathbf{Cl}_{0.66}\cdot n\mathbf{H}_{2}\mathbf{O}$						
0		9.4	0	9.4	0	9.4	0	9.4	0	
0.5		39.1	0.62	47.7	0.84	51.4	0.88	_	-	
1		42.0	0.69	47.7	0.84	51,7	0.89	52.3	0.90	
2		48.0	0.81	52.5	0.94	54.7	0.95	54.5	0.95	
4		48.0	0.81	54.1	0.98	56.0	0.98	55.5	0.97	
6		52.0	0.90	55.0	1.0	56.9	1.0	56.5	1.0	

TABLE 1

Kinetics of isotopic exchange $^6\text{Li}-^7\text{Li}$ in the systems LiCl–[Li_{0.92}Al_2(OH)_6]Cl_{0.92} \cdot nH_2O and LiCl–[Li_{0.66}Al_2(OH)_6]Cl_{0.66} \cdot nH_2O at different temperature values

sized from mechanically activated aluminium hydroxide under comparable experimental conditions is an order of magnitude higher than the exchange level for double hydroxide obtained from crystalline gibbsite. The double aluminium and lithium hydroxide synthesized from mechanically activated aluminium hydroxide consists of micron sized aggregates formed by submicron particles [16]. The specific surface area of the double hydroxide is equal to $5-6 \text{ m}^2/\text{g}$. The average particle size was determined by means of formula

$$D = 6/(\rho S) \tag{4}$$

where ρ is the density of double hydroxide; *S* is the specific surface area. Basing on the data obtained ($D = 0.5-0.6 \mu$ m) it could be assumed that one of the reasons for the differences in the level of isotopic exchange consists in a difference in the dispersion level of double hydroxides. Unfortunately, basing on the data obtained, it is difficult to evaluate the diffusion coefficient, since even at the lowest temperature used for the isotopic exchange experiments (40 °C) and at the minimum duration of the experiment (0.5 h) the exchange level is sufficiently high (more than 60 %).

CONCLUSION

The data obtained concerning the kinetics of lithium isotopic exchange in the aqueous solution of lithium chloride – the chloride form of aluminium and lithium double hydroxide allow one to suggest that the rate of the process at a low exchange level is limited by the process of diffusion through the solid phase. The faster isotopic exchange rate revealed for double hydroxide synthesized from mechanically activated aluminium hydroxide, could be, to all appearance, connected with a high dispersion level of the compound, which determines the perspective of its use in practical lithium isotope separation.

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